



Photoinduced electron transfer processes of (E)-9-(4-nitrostyryl)anthracene in non-polar solvent medium: generation of long-lived charge-separated states[§]

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Abstract. In the present study, photoinduced electron transfer (PET) dynamics between N,N-diethylaniline (DEA) and (E)-9-(4-nitrostyryl)anthracene (An-NO₂) in a non-polar solvent medium {methylcyclohexane (MCH)}, has been investigated. The rate constant of back electron transfer (k_{BET}) for the An-NO₂ – DEA pair was $\sim 3.8 \times 10^5 \text{ s}^{-1}$ which is *ca.* 2 orders of magnitude *less* compared to the anthracene (An)-DEA (control) system. The results indicate that long-lived charge separated species can be generated using the design strategy used herein by achieving resonance stabilization of the excited state (acceptor) radical *via* conjugation.

Keywords. Photoinduced electron transfer; π -conjugated system; back electron transfer; long-lived charge-separated states.

1. Introduction

In the past decades, organic donor – acceptor (D-A) molecules have attracted significant attention due to their potential applications in photovoltaic cells and optoelectronic devices.^{1–5} For such applications, there is a need for designing donor-acceptor systems that would hinder charge-recombination upon photoexcitation,^{6,7} so that the back electron transfer process is slowed down leading to the generation of long-lived charge separated states. Long-lived charge separated species find their applications in various emerging fields of research such as solar cells, energy conversions and heterogeneous photocatalysis.^{8–10}

Charge-separated species *viz.*, radical cations and radical anions are the primary photoproducts generated *via* intra- as well as inter-molecular photoinduced electron transfer (PET) processes.^{11–14} An important and challenging area of research in this field is to devise strategies for stabilizing the charge-separated states formed *via* PET processes. Reports show that

bimolecular PET processes carried out in constrained media like micelles and zeolites, generate long-lived charge separated states owing to the reduced rate of back electron transfer.^{15,16} In a similar way, designing of dyad or triad systems with proper structural attributes have been found to significantly lower the rate of intramolecular back electron transfer.¹⁷

That extended conjugation in a molecule enhances resonance stabilization of a radical center in it, is a known concept in chemistry. Thus we propose that the radical anion generated *via* transfer of electron from donor to acceptor, would be stable if the acceptor system has an extended π -conjugation that is capable of de-localizing the negative charge within the molecule *via* a '*push-pull*' mechanism. In a recent work from our group, we have established this hypothesis for two highly conjugated derivatives of pyrene and anthracene, namely (E)-4-(2-(pyren-1-yl)vinyl)benzotrile (PyCN) and (E)-4-(2-(anthracen-9-yl)vinyl)benzotrile (AnCN).¹⁸ In the present work, we extend this particular hypothesis to another extremely well-studied organic

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[§]Dedicated to Professor M V George on the occasion of his 90th Birth Anniversary.

D- π -A system *namely*, (E)-9-(4-nitrostyryl)anthracene (An-NO₂).^{19–23} We hypothesize that An-NO₂ as an electron acceptor can generate long-lived charge separated species *via* PET due to the increased feasibility of charge delocalization in it.

It is well known that in highly non-polar solvent medium like hexane and methylcyclohexane (MCH), An-NO₂ emits from its excited singlet state (S₁), whereas with slight increase in solvent polarity, significant intramolecular charge transfer (ICT) occurs in the excited state.^{19–23} In order to avoid any discrepancies arising from structural distortions in the excited state due to ICT, we have carried out the PET studies in methylcyclohexane (MCH). Steady state and time resolved luminescence quenching studies have been carried out to determine the bimolecular quenching constant (k_q). Nanosecond laser flash photolysis experiments have been carried out to verify the formation of the transient radical ions and to determine the rate constant of back electron transfer. The obtained results have been compared with that of the anthracene (An) – DEA system.

2. Experimental

2.1 Materials

All commercially available reagents and solvents were used without further purification. 4-nitrobenzyl bromide and all UV-grade solvents (i.e., methylcyclohexane and THF) were bought from Spectrochem Pvt. Ltd, India. Triphenylphosphine and 9-anthracenecarboxaldehyde were bought from Sigma Aldrich (U.S.A). Potassium tertiary butoxide was obtained from Avra Synthesis Pvt. Ltd., India. N, N-diethylaniline was bought from Merck. Reactions were carried out in oven-dried glassware (i.e., round bottom flasks, vials, and NMR tubes) under nitrogen atmosphere.

2.2 UV-visible absorption studies

A JASCO V-660 spectrophotometer was used for carrying out the UV-visible absorption studies. All samples were taken in a square-shaped two-faced transparent quartz cuvette having a path length of 1 cm. All the experiments were carried out at ambient temperature. Concentration dependent UV-visible experiments were carried out keeping the concentration of An-NO₂ constant at 40 μ M while the concentration of DEA was varied in between 0.024 M– 0.168 M.

2.3 Steady state luminescence experiments

All the steady state luminescence experiments were carried out in a Horiba Jobin Yvon Fluoromax-4 instrument using a four-side transparent quartz cuvette. Luminescence quenching experiments were carried out with a series of DEA

solutions with varying concentrations (0.024 M to 0.168 M), keeping the excitation/emission slit widths at 2/2.

2.4 Time-resolved luminescence decay measurements

Time resolved luminescence measurements were carried out in a Horiba Jobin Yvon Fluorocube instrument in a time correlated single photon counting (TCSPC) arrangement using a 405 nm LED with a pulse repetition rate of 1 MHz as the light source. The Instrument Response Function (IRF) was collected using a scatterer (Ludox AS40, colloidal silica, Sigma Aldrich). The full width at half maximum for the 405 nm LED light source is approximately 0.5 ns including detector response. The wavelength was fixed at near the emission maximum and the excited state decay of the samples was collected and the decay was fitted using the IBH software DAS6 according to the following equation:

$$I(t) = \sum A_i \exp(-t/\tau_i)$$

τ_i = luminescence lifetime, A_i = the amplitude of the corresponding decay.

2.5 Laser flash photolysis studies

Transient absorption spectra (TAS) were recorded using a nanosecond laser flash photolysis instrument (Applied Photophysics, U.K.). To photo excite the samples, the third harmonic of a Q-switched Nd: YAG laser (Quanta Ray, Lab 150, Spectra Physics, USA) was used. The signals from the transients were probed using a 150 W pulsed xenon lamp, a Czerny – Turner monochromator, and Hamamatsu R-928 photomultiplier tube as a detector. The pulse width of the laser light was 8 ns. The transient signals were captured using an Agilent infinium digital storage oscilloscope followed by the transfer of all the data to the computer for further analysis. Before recording the TAS the samples were purged with Argon gas for 30 minutes.

3. Results and Discussion

The structure of the aromatic amine {N,N-diethylaniline (DEA)} and the conjugated anthracene derivative, (E)-9-(4-nitrostyryl)anthracene {An-NO₂} is shown in Chart 1. The synthesis details and scheme for An-NO₂ has been provided in the Supplementary Information along with the characterization (¹H, ¹³C and HR-MS) data of An-NO₂ (Scheme S1 1.1, Supplementary Information).

3.1 Steady-state luminescence quenching studies

In MCH, An-NO₂ exhibits a structured absorption spectrum with the maxima around 390 nm. Upon addition of DEA, the absorbance maxima did not show any shift. Further, no changes were observed in the

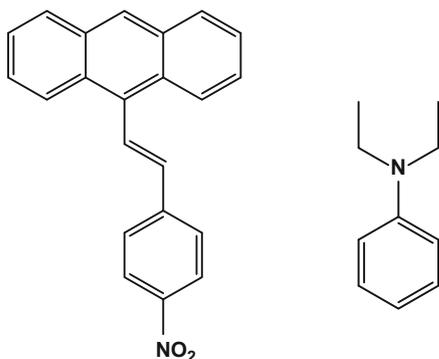


Chart 1. The structure of the electron acceptor (E)-9-(4-nitrostyryl)anthracene (An-NO₂) on the left and the structure of the electron donor N,N-diethylaniline (DEA) on the right.

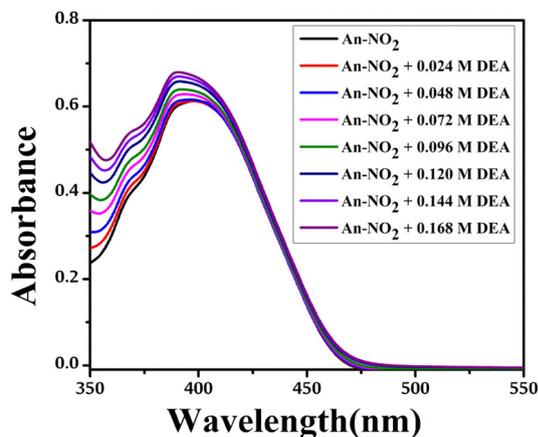


Figure 1. The UV-Visible absorption spectra of An-NO₂ [40 μM] with increasing concentration of N,N-diethylaniline (DEA) [0.024 M–0.168 M] in methylcyclohexane (MCH).

shape of the absorption spectrum upon addition of DEA (Figure 1). The small enhancement in absorbance in the region ≤ 425 nm is due to the absorbance of the quencher DEA. Thus, we conclude that there is no significant interaction between the donor and the acceptor molecule in their ground state.

When excited at 400 nm, An-NO₂ exhibits an emission maximum around 505 nm. Upon addition of the quencher DEA, the emission intensity reduced significantly suggesting a strong interaction between excited singlet S₁ state of An-NO₂ with the amine, DEA (Figure 2). It is to be noted that no exciplex emission has been observed upon addition of the quencher, which is in contrast to the control system *viz.*, anthracene (An) - DEA in non-polar solvents.^{24,25}

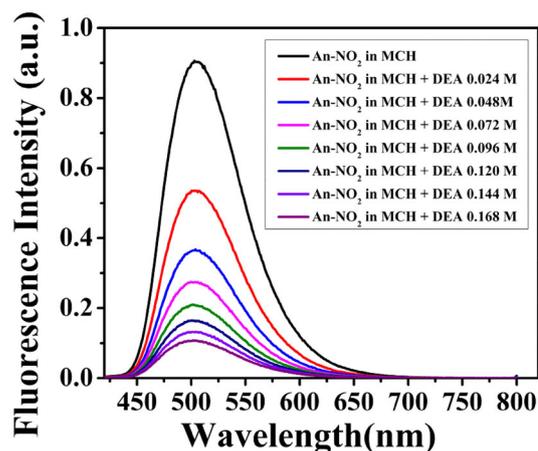


Figure 2. The steady-state luminescence quenching studies of An-NO₂ [40 μM] in methylcyclohexane (MCH) with increasing concentration of the quencher N,N-diethylaniline (DEA) [0.024 M–0.168 M]. The excitation wavelength (λ_{ex}) = 400 nm. [Note: no red-shifted band has been observed with increased DEA concentration showing that no exciplex formation has taken place upto this particular concentration of DEA].

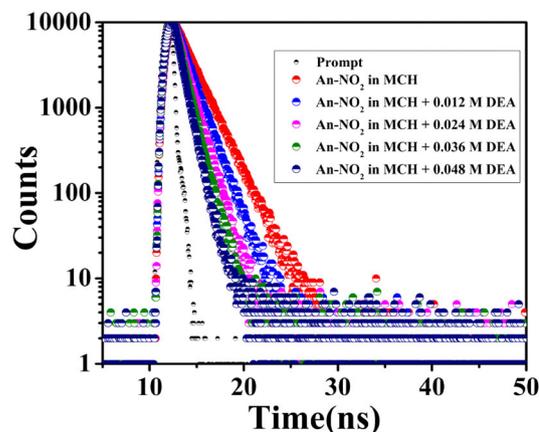


Figure 3. The time-resolved luminescence quenching studies of An-NO₂ [40 μM] in methylcyclohexane (MCH) with increasing concentration of the quencher; N,N-diethylaniline (DEA) [0.012 M–0.048 M]. The excitation wavelength (λ_{ex}) is 405 nm. The collection wavelength (λ_{coll}) is 500 nm.

3.2 Time-resolved luminescence quenching studies

An-NO₂ exhibits a lifetime of 1.8 ns in MCH which reduces significantly on addition of the quencher. The lifetime decay profiles are given in Figure 3 and the lifetime quenching data is summarized in Table 1.

From the steady-state luminescence quenching studies, we rule out the possibility of resonance energy

Table 1. Luminescence lifetime values of An-NO₂ in presence of various concentrations of DEA (0.012 M–0.048 M), λ_{ex} = 405 nm, λ_{coll} = 500 nm.

[DEA] (M)	τ (in ns)	χ ²
0	1.80	1.03
0.012	1.36	1.02
0.024	1.08	1.03
0.036	0.90	1.07
0.048	0.74	1.20

transfer from excited An-NO₂ to DEA since there is no significant overlap between the emission spectrum of An-NO₂ and absorption spectrum of DEA. Since DEA is a tertiary amine the possibility of an excited state proton transfer can also be ruled out. The results taken together point towards the fact that the observed luminescence quenching is due to PET.

3.3 Stern-Volmer analysis

The steady-state (SS) and time-resolved (TR) Stern-Volmer plots for the An-NO₂ and DEA pair was plotted and the quenching constant (k_q) was determined. The plots have been presented as Figures S1 and S2, Supplementary Information. The comparable k_q values (within the range of experimental error) obtained in the SS and TR Stern Volmer analysis *viz.* 2.2 × 10¹⁰ M⁻¹s⁻¹ and 1.6 × 10¹⁰ M⁻¹s⁻¹, respectively, asserts the dynamic nature of the quenching. Further, it is known that the value of k_q lies in the range of 10⁹–10¹⁰ M⁻¹s⁻¹ in the diffusion-controlled regime.²⁶ Thus, we conclude that the observed luminescence quenching of An-NO₂ is diffusion-controlled.

3.4 Calculation of the free energy change associated with forward electron transfer (PET) and back electron transfer (BET) processes

To realize the thermodynamic feasibility of the forward electron transfer process (PET) between DEA and An-NO₂, the free energy of PET (ΔG_{PET}) has been calculated using the oxidation potential of the donor (DEA) and reduction potential of the acceptor (An-NO₂). The oxidation potential of DEA in acetonitrile has been obtained from literature^{27,28} and reduction potential of An-NO₂ was determined in acetonitrile [Figure S3, Supplementary Information] and those values have been utilized to evaluate the free energy of PET in methylcyclohexane according to the modified Rehm-Weller equation.²⁹

$$\Delta G_{PET} = E^0(D^+/D) - E^0(A/A^-) - E^{00}$$

$$- \left[\frac{e^2}{2 * 4\pi \epsilon_0} \left(\frac{1}{r_D} + \frac{1}{r_A} \right) \left(\frac{1}{37} - \frac{1}{\epsilon_s} \right) \right] - \frac{e^2}{4 \pi \epsilon_0 d_{cc}} \quad (1)$$

where, E⁰(D⁺/D) = 0.76 V [vs Ag/Ag⁺ (satd. KCl)] and E⁰(A/A⁻) = -1.25 V [vs Ag/Ag⁺ (satd. KCl)] are the oxidation potential of the donor and reduction potential of the acceptor, respectively (in acetonitrile), E⁰⁰ = the singlet energy of the acceptor = 2.68 eV, e = charge of an electron = 1.602 × 10⁻¹⁹ C, ε₀ = permittivity of free space, ε_s = dielectric constant of the solvent where we want to measure the feasibility of electron transfer (methylcyclohexane with ε_s = 2.02), r_D = 0.4 nm and r_A = 0.6 nm are the radii of the donor and acceptor, respectively, and d_{cc} = the centre to centre distance of the donor and the acceptor in the encounter complex (d_{cc} ~ r_D + r_A). The E⁰⁰ value for An-NO₂ was calculated from the point of intersection of the absorption and emission spectrum. The calculated ΔG_{PET} value was negative *viz.* -0.73 eV which explains the feasibility of the PET process.

Additionally, we calculated the driving force for the back electron transfer process (ΔG_{BET}) *viz.* -1.95 eV utilizing the value of E⁰⁰ and ΔG_{PET} according to the following formula:^{30,31}

$$\Delta G_{BET} = -E^{00} - \Delta G_{PET} \quad (2)$$

In order to observe the formation of the charge separated states *via* PET, nanosecond laser flash photolysis experiments were carried out.

3.5 Laser flash photolysis studies

The transient absorption spectrum of An-NO₂ [40 μM] in MCH exhibits two sharp peaks centered at 520 nm and 540 nm with a lifetime of 1.8 ± 0.1 μs. These two peaks are assigned to the T₁-T_n transitions of An-NO₂ in MCH. The decay rate constant for the T₁-T_n transition is *ca.* 5.5 × 10⁵ s⁻¹ (Figure 4).

The TAS spectral envelope of An-NO₂ changes in presence of the quencher DEA [0.168 M] wherein, it exhibits two sharp peaks centered around 460 nm and 510 nm, respectively. These peaks exhibit a lifetime of 2.6 ± 0.1 μs. Based upon literature, we can assign the 460 nm peak to the DEA radical cation.^{18,32} Thus, the 510 nm peak is supposedly due to the An-NO₂ radical anion. The decay rate constants corresponding to the transient lifetimes of the ion-pair is roughly equal and is ~ 3.8 × 10⁵ sec⁻¹. We assign the decay rate constants as the rate constant for back electron transfer (k_{BET}) considering the ion-pairs do not participate in any other excited state processes. It is to be noted

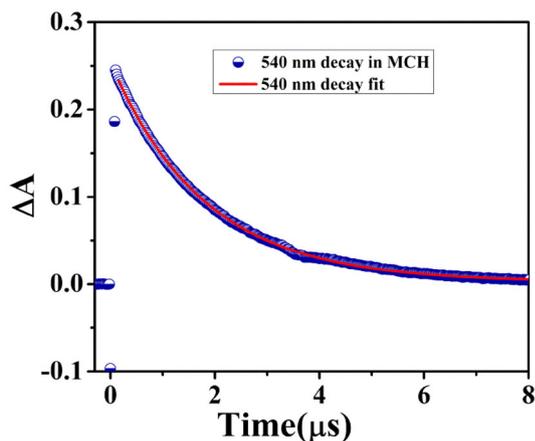


Figure 4. The 540 nm decay of An-NO₂ in MCH ($\lambda_{\text{ex}} = 355$ nm) revealing a T₁-T_n decay rate constant of $\sim 5.5 \times 10^5$ s⁻¹.

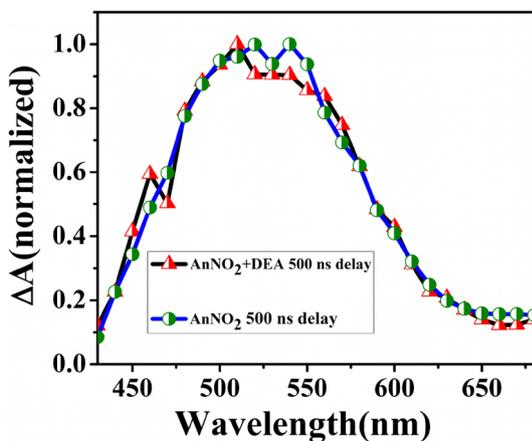


Figure 5. The normalized ΔA spectrum for An-NO₂ [40 μM] and An-NO₂ + DEA [0.168 M] at 500 ns delay clearly revealing the change in the TA spectral profile. The former spectrum reveals two peaks centered around 540 nm and 520 nm which can be assigned as the T₁-T_n transitions of An-NO₂. In presence of DEA, the later spectrum reveals two peaks at 510 nm and 460 nm which can be assigned as the An-NO₂ radical anion and DEA radical cation, respectively.

that the formula $k_{\text{BET}} = 1/\tau_{\text{radical}}$ has been used for the calculation of the back electron transfer rate constant value. Figure 5 shows the ΔA normalized spectra of An-NO₂ in MCH at 500 ns delay, in the presence and absence of DEA, clearly revealing the differences. Figure 6 shows the 510 nm decay for An-NO₂ + DEA system. It is to be noted that in presence of DEA, the ΔA values for the T₁-T_n transitions significantly reduces which also enunciates a significant excited state interaction between An-NO₂ and DEA leading to a reduction in the triplet population.

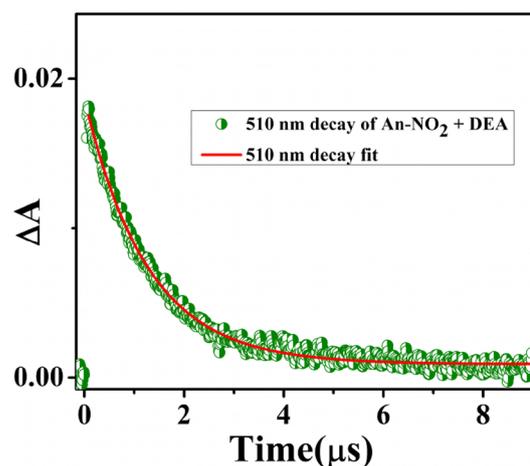


Figure 6. The 510 nm decay of An-NO₂ + DEA revealing a back electron transfer rate constant (k_{BET}) of 3.8×10^5 s⁻¹.

Similar experiments with the control system An-DEA in MCH, revealed the growth of a new band around 350–370 nm. From literature reports, this band can be assigned as the anthracene radical anion.^{33,34} The calculated rate constant for the back electron transfer process for An-DEA was found to be ($\sim 1 \times 10^7$ sec⁻¹), which is significantly faster compared to our system. The transient absorption spectra of anthracene in presence and absence of DEA has been shown (Figures S4–S5, Supplementary Information). The 350 nm decay fit has been shown in Figure S6 (Supplementary Information).

The free-energy change for the BET process for An-DEA is -1.35 eV whereas for An-NO₂ it is -1.95 eV (Table 2). In terms of the energetics of the back electron transfer process, k_{BET} (An-NO₂ + DEA) should be *higher* than k_{BET} (An + DEA). Thus, we conclude that the BET process is not activation controlled. The enhanced stability of the charge-separated states for the An-NO₂-DEA pair is attributed to the increased stability of the An-NO₂ radical anion (compared to the anthracene radical anion) *via* delocalization of the charge over the extended π -conjugated structure.

Additionally, PET studies of An-NO₂ and DEA has been carried out in a relatively polar solvent tetrahydrofuran (THF). The results have been presented in the supplementary information (Figures S7–S11). Since, in THF, An-NO₂ emits from the ICT state and not from its excited singlet state as in MCH, no comparison of the PET dynamics has been done with the control molecule anthracene. However, the k_{BET} value has been calculated which is $\sim 1.36 \times 10^5$ s⁻¹ which is slightly *less* compared to the k_{BET} value in MCH. This shows that with

Table 2. The tabulated parameters *viz.* E^{00} , r_D , r_A , d_{cc} , ΔG_{PET} , ΔG_{BET} , k_{BET} for An-NO₂-DEA and anthracene (An)-DEA.

System	E^{00} (eV)	r_D (nm)	r_A (nm)	d_{cc} (nm)	ΔG_{PET} (eV)	ΔG_{BET} (eV)	k_{BET} (s ⁻¹)
An-NO ₂ and DEA	2.68	0.40	0.60	1.0	-0.73	-1.95	3.8×10^5
Anthracene and DEA	3.30	0.40	0.46	0.85	-1.95	-1.35	1×10^7

increase in solvent polarity, the solvation of the radical species gets enhanced, leading to a greater stabilization of the charge-separated states.

4. Conclusions

The photoinduced electron transfer from N,N-diethylaniline (DEA) to (E)-9-(4-nitrostyryl)anthracene (An-NO₂) in a non-polar solvent medium *viz.* methylcyclohexane (MCH) has been studied. It has been observed that the luminescence quenching is diffusion-controlled. Unlike anthracene, no exciplex formation has been observed for An-NO₂. The radical ion species formed as a result of the PET process has been assigned. The rate constant for the back electron transfer process (k_{BET}) has been calculated using the formula $k_{BET} = 1/\tau_{\text{radical}}$. It has been observed that the rate constant for the back electron transfer process is ~ 2 orders of magnitude slower in case of An-NO₂/DEA when compared with anthracene/DEA. We conclude that the presence of extended π -conjugated structure leads to efficient delocalization of charge in case of An-NO₂, thus generating long-lived charge separated states *via* intermolecular PET processes.

Supplementary Information (SI)

The synthesis and characterization data of An-NO₂ *viz.*, ¹H-NMR, ¹³C-NMR and HR-MS spectra; the steady-state and time-resolved Stern-Volmer plots; the cyclic voltammetry study of An-NO₂ in acetonitrile; the ΔA vs wavelength plot for anthracene in the absence and in presence of DEA; ΔA vs time plot for the BET rate constant for An-DEA system; PET data for An-NO₂-DEA in THF; excitation spectra of An-NO₂ in the absence and in presence of DEA. Supplementary Information is available at www.ias.ac.in/chemsci.

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